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(54) LITHIUM ION CONDUCTIVE GLASS CERAMICS AND CELL AND GAS SENSOR USING SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To easily produce thermally and chemically stable lithium ion conductive glass ceramics having high conductivity at room temp. and to obtain a cell and a gas sensor using the glass ceramics.
SOLUTION: Raw glass contg., by mol, 35-40% P_2O_5, 0-15% SiO_2, >0 to 50% GeO_2 0 to <50% TiO_2 (25%≤ GeO_2+TiO_2≤50%), 0-10% ZrO_2, 0.5-15% M_2O_3 (M is A1 and/or Ga) and 10-25% Li_2O is melted, molded and heat-treated. By this heat treatment, a crystalline phase of $Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ (0<X≤0.8 and 0≤Y<1.0) is deposited to obtain the objective glass ceramics. A lithium cell. and a gas sensor using the glass ceramics exhibit satisfactory characteristics.

CLAIMS

[Claim(s)]

[Claim 1]By mol%, 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -50%, $TiO_2$0 -<50%, However, 25 to 50% of GeO_2+TiO_2, 0 to 10% of ZrO_2, One sort or two-sort $Li_2$0 chosen from 0.5 to 15% of M_2O_3 however M=aluminum, and Ga 10 to 25%, . Pass a heat treatment process after melt molding in original glass containing a presentation of ******. Lithium-ion-conductivity crystallized glass depositing a $Li_{1+X}M_X$(germanium$_{1-Y}$Ti$_Y$) $_{2-X}$(PO_4) $_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase.

[Claim 2]By mol%, 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, $TiO_2$0 -<45%, However, 25 to 45% of GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of aluminum$_2O_3$, and $Li_2$0 10 to 25%, . Pass a heat treatment process after melt molding in original glass containing a presentation of ******. Lithium-ion-conductivity crystallized glass depositing a Li_{1+X}aluminum$_X$(germanium$_{1-Y}$Ti$_Y$) $_{2-X}$(PO_4) $_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase.

[Claim 3]By mol%, 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, $TiO_2$0 -<45%, However, 25 to 45% of GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of Ga_2O_3, and $Li_2$0 10 to 25%, . Pass a heat treatment process after melt molding in original glass containing a presentation of ******. Lithium-ion-conductivity crystallized glass depositing a $Li_{1+X}Ga_X$(germanium$_{1-Y}$Ti$_Y$) $_{2-X}$(PO_4) $_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase.

[Claim 4]A solid electrolyte for lithium cells using lithium-ion-conductivity crystallized glass of a statement for claims 1-3.

[Claim 5]A solid electrolyte for gas sensors using lithium-ion-conductivity crystallized glass of a statement for claims 1-3.

[Claim 6]A lithium cell using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3 [Claim 7]A gas sensor using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Ionic conductivity of this invention is high, and is thermally and chemically stable, and manufacture is related with easy lithium-ion-conductivity crystallized glass.
[0002]
[Description of the Prior Art]Progress of the electronics in recent years is remarkable, and the miniaturization of electronic equipment, a weight saving, and highly efficient-ization are progressing quickly. Then, as these power supplies for apparatus, development of a long lasting cell is strongly desired with high energy density, and the expectation for a lithium ion battery is large especially every day.
[0003]Since the oxidation-reduction potential of lithium elements of Li/Li^+ is the highest in all metal and the mass per mol is dramatically small, the lithium cell can obtain high energy density from other cells. By using a lithium ion conductive solid electrolyte, it becomes possible to make an electrolyte part thin, and the thin weight saving of the cell itself can be carried out, and it becomes possible to raise the energy density per volume greatly.

[0004]In addition to a miniaturization and thin-film-izing of a cell being difficult for the lithium ion battery put in practical use now, since an electrolyte is organic electrolysis liquid, we are anxious about liquid leakage or the danger of ignition. If it is transposed to an inorganic solid electrolyte, it will be thought that a reliable and extremely stable totally-solid battery can be constituted.
[0005]The choke damp emitted by combustion of a fossil fuel is the main factor of the greenhouse effect which poses a problem in recent years.
For this reason, the continuous surveillance of choke-damp concentration is needed.
Therefore, in order that establishment of these detection systems may maintain the comfortable living environment of future human society, the importance is increasing.
[0006]Although the choke-damp detection system with which practical use is presented has a common type using infrared absorption now, a device is large-sized, and is expensive and it has in contamination the fault that it is weak. Therefore, these days, research of the compact carbon dioxide gas sensor which used the solid electrolyte is done briskly. In it, many researches using a lithium ion solid electrolyte are reported.
[0007]However, in order to realize these, conductivity is high, it is chemically stable, and development of a solid electrolyte strong against heat is indispensable. As what conductivity is high in a solid electrolyte by the present, and exceeds 10^{-3}S/cm at a room temperature, A Li_3N single crystal [Applied PhysicsLetters, 30(1977)P.621-622], $LiI-Li_2S-P_2S_5$ [Solid State Ionics, 5(1981)P.663], $LiI-Li_2S-SiS_4$[J. Solid State Chem. and 69(1987)P.252], Although the glass of a $LiI-Li_2S-B_2S_3$ [Mat.Res.Bull., 18(1983)P.189] system is known, such materials are difficult to produce, chemical stability is not good, either, and heat has the fault that it is weak. Since decomposition voltage is low especially when using it as an electrolyte of a solid state battery, it has the fatal fault that high terminal voltage cannot be taken.
[0008]On the other hand, the possibility of utilization is high if a room temperature shows high conductivity, since an oxide lithium solid electrolyte does not have the above faults, and decomposition voltage is also higher than 3V. In oxide glass, increasing conductivity is known by increasing the concentration of a lithium ion. However, even if it uses rapid quenching for the purpose of vitrification, for example, there is a limit in the increase in the concentration of a lithium ion, and what has the high conductivity in a room temperature has not reached 10^{-}

^{6}S/cm.
[0009]Although JP,8-239218,A has the statement of the gas sensor which used the lithium-ion-conductivity glass thin film, That in which the conductivity of the lithium-ion-conductivity glass thin film by this has 6.1x10 $^{-7}$S/cm from 1.7x10 $^{-7}$ and not a by no means high thing but higher conductivity is needed.
[0010]About oxide ceramics (sintered compact), many examples which have high lithium ion conductivity are reported. A Li_4GeO_4-Li_3VO_4 system For example, 4x10 $^{-5}$S/cm [Mat.Res.Bull., 15(1980)P.1661], $Li_{1-X}M_XTi_{2-X}(PO_4)_3$ (M=aluminum, Ga, Cr, etc.) -- 7x10 $^{-4}$S/cm[-- J. -- Electrochem.Soc. and 137(1990)P.1023]. A Li_{1+X}aluminum$_X$germanium$_{2-X}(PO_4)_3$ system 1.3x10 $^{-4}$S/cm[Proceedings of 8 th international meetingon lithium. The conductivity in the room temperature batteries, June 16-21-1996, Nagoya, Japan, and P.316-317] is shown. Although oxide ceramics are advantageous in respect of conductivity compared with oxide glass, a manufacturing process is complicated and the moldability has the fault that it is bad and thin-film-izing is difficult.
[0011]
[Problem(s) to be Solved by the Invention]As stated above, the conventional lithium ion solid electrolyte had low conductivity, handling was difficult, and it had the technical problem that thin-film-izing was difficult. This invention solves these technical problems, the crystallized glass which has high lithium ion conductivity in a room temperature is provided, and it aims at realizing a highly efficient lithium cell and gas sensor further using this crystallized glass.
[0012]
[Means for Solving the Problem]As mentioned above, in ceramics, conductivity of a 10 $^{-4}$S/cm stand is found out at a room temperature. However, a stoma and a grain boundary which can never be lost exist in an inside of ceramics. These existence brings about decline in conductivity. Since a stoma can be lost and being improved also about a grain boundary will be expected if crystallized glass including a conductive crystal is obtained, it is expectable to obtain a solid electrolyte which has higher conductivity. Since various shape and thin film-ization are attained taking advantage of the characteristic of glass in the case of crystallized glass, a merit more practical than ceramics produced with a sintering process is large.
[0013]As a result of repeating research wholeheartedly based on such a view, this invention person P_2O_5, SiO_2, GeO_2, TiO_2, ZrO_2, and M_2O_3. Glass containing one sort chosen from M=aluminum and Ga or a (two-sort [however,]) Li_2O ingredient is produced, Through a heat treatment process by depositing conductive crystal $Li_{1+X}M_X$(germanium$_{1-Y}Ti_Y$)$_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) from glass, A lithium cell and a gas sensor which succeeded in obtaining crystallized glass which has high lithium ion conductivity in a room temperature, and used this came to find out that the good characteristic is shown.
[0014]Namely, the invention according to claim 1 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -50%, $TiO_2$0 -<50%, However, 25 to 50% of GeO_2+TiO_2, 0 to 10% of ZrO_2, One sort or two-sort Li_20 chosen from 0.5 to 15% of M_2O_3 however M=aluminum, and Ga 10 to 25%, It is characterized by original glass containing a presentation of ****** depositing a $Li_{1+X}M_X$(germanium$_{1-Y}Ti_Y$)$_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0015]The invention according to claim 2 is mol%, and 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, 25 to 45% of $TiO_2$0 -<45%, however GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of aluminum$_2O_3$, Li_20 Original glass containing a presentation of the range of 10 to 25%**, It is characterized by depositing a Li_{1+X}aluminum$_X$(germanium$_{1-Y}Ti_Y$)$_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0016]The invention according to claim 3 is mol%, and 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, 25 to 45% of $TiO_2$0 -<45%, however GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of Ga_2O_3, Li_20 Original glass containing a presentation of the range of 10 to 25%**, It is characterized by depositing a $Li_{1+X}Ga_X$(germanium$_{1-Y}Ti_Y$)$_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0017]The invention according to claim 4 is characterized by using lithium-ion-conductivity crystallized glass of a statement for claims 1-3 in a solid electrolyte for lithium cells, [0018]The invention according to claim 5 is characterized by using lithium-ion-conductivity crystallized glass of a statement for claims 1-3 in a solid

electrolyte for gas sensors, [0019]The invention according to claim 6 is characterized by using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3 in a lithium cell, [0020]The invention according to claim 7 is characterized by using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3 in a gas sensor.

[0021]A presentation of crystallized glass of this invention can be displayed by an oxide basis like original glass. A reason which limited a presentation of crystallized glass as mentioned above is explained below.

[0022]Original glass containing the above-mentioned presentation through a heat treatment process after melting cooling by depositing a $Li_{1+X}M_X(germanium_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase, With the conventional ceramics, precise crystallized glass which is not obtained can be obtained and, moreover, the crystallized glass shows very high lithium ion conductivity with a room temperature. Although a $Li_{1+X}M_X(germanium_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ crystal phase deposits also in presentation fields other than the above, since the rate is very low, conductivity is small and application to practical use is difficult.

[0023]Also in the above-mentioned ingredient, especially M_2O_3 (one sort chosen from M=aluminum and Ga or two sorts), By being an important ingredient and adding this M_2O_3 ingredient 0.5 to 15% in an improvement of the melting nature of glass, and thermal stability, Melting nature and thermal stability of glass improved, and conductivity which exceeds 10^{-4}S/cm to a still more surprising thing in a composition range where conductivity of crystallized glass after heat treatment is also wide was shown. If an M_2O_3 ingredient is not filled to 0.5%, although vitrification is carried out, if melting nature and thermal stability of glass are bad and exceed 15%, On the contrary, melting nature falls, conductivity of crystallized glass after heat treatment also falls remarkably, and, below in 10^{-6}S/cm, conductivity becomes. A range in which said M_2O_3 ingredient is more preferred than ** is 1 to 14%, and especially a desirable range is 3 to 12%.

[0024]GeO_2 is an ingredient indispensable to formation of glass, and is also a constituent of a conductive crystal phase. if the amount of GeO_2 increases, although it becomes easy to form glass, since the effect is small, when the desired characteristic is not obtained but 50-mol% is exceeded conversely, said conductive crystal phase becomes difficult to deposit less than [25mol%] indeed. It is replaceable with TiO_2 and GeO_2 is possible for the substitutional rate to about 100%. And improvement in Li-ion conductivity is also found by substitution. They must be GeO_2=0<-50% from these things, TiO_2=0-<50%, however GeO_2+TiO_2=25-50%. a desirable range -- GeO_2=0<-45% and TiO_2=0-<45% -- however, It is GeO_2+TiO_2=25-45% and especially desirable ranges are GeO_2=0<-40%, TiO_2=0-<40%, however GeO_2+TiO_2=28-40%.

[0025]While the addition of SiO_2 can raise thermal stability of original glass, Si^{4+} ion dissolves to said crystal phase, and contributes it also to improvement in Li^+ ionic conductivity. However, since conductivity will fall on the contrary if the quantity exceeds 15%, it must be made to 15% or less. A desirable range is 13% or less, and especially a desirable range is 10% or less.

[0026]Addition of ZrO_2 has an effect which promotes generation of this crystal phase. However, since the devitrification-proof nature of original glass falls remarkably, creation of uniform original glass will become difficult and also conductivity will also fall rapidly if the quantity exceeds 10%, it must be made to 10% or less. A desirable range is 8% or less, and especially a desirable range is 5% or less.

[0027]Although it is also possible to be divalent metals, such as trivalent metals, such as B, In, Sc, Fe, and Cr, and Mg, Ca, Sr, Ba, and Zn, and to replace a part of aluminum or Ga ingredient, those quantity should be made less than 10mol%. If it adds more, production of original glass will become difficult or conductivity will fall remarkably.

[0028]In order to improve the melting nature of glass further, it is also possible to add As_2O_3, Sb_2O_3, Ta_2O_3, CdO, PbO, etc., but those quantity should be restricted to 3% or less. Addition of more than it will reduce conductivity remarkably in connection with an addition.

[0029]

[Embodiment of the Invention]The lithium-ion-conductivity crystallized glass of this invention can be manufactured by the following methods. That is, after carrying out specified quantity weighing of each starting material and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an

electric furnace. In heating and dissolving, a raw material is first disassembled at 700 **, and gas constituents are evaporated. Next, temperature is raised to 1300-1450 **, and at the temperature, it holds for 1 to 2 hours, and dissolves. Then, the cast of the melting glass is carried out on a griddle, and tabular glass is produced. In this way, the obtained glass is heat-treated at 600-1000 ** for 12 to 24 hours. By the above process, the crystallized glass with high lithium ion conductivity in which $Li_{1+X}M_X(\text{germanium}_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ deposited as a main crystal phase is obtained.

[0030]

[Example]This invention is not limited by these examples although a concrete example explains this invention below.

[0031][Example 1] $NH_4H_2PO_4$, GeO_2, aluminum$(OH)_3$, and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 20.0% of Li_2 P_2O_5=37.5%, GeO_2=35.0%, and aluminum$_2O_3$=7.5% by mol%, and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1300 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 520 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 750 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is $Li_{1+X}\text{aluminum}_X\text{germanium}_{2-X}(PO_4)_3$. It is shown in drawing 1 of the X diffraction pattern of this crystallized glass. The crystallized glass showed high conductivity called 4.0×10^{-4}S/cm at the room temperature.

[0032][Example 2] $NH_4H_2PO_4$, GeO_2, and Ga_2O_3 and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 17.5% of Li_2 P_2O_5=37.5%, GeO_2=40.0%, and Ga_2O_3=5.0% by mol%, and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1300 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 510 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 800 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is $Li_{1+X}Ga_X\text{germanium}_{2-X}(PO_4)_3$. The crystallized glass showed high conductivity called 2.0×10^{-4}S/cm at the room temperature.

[0033][Example 3] $NH_4H_2PO_4$, GeO_2, TiO_2, and aluminum$_2O_3$ and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 17.5% of Li_2 P_2O_5=37.5%, GeO_2=30.0%, TiO_2=10%, and aluminum$_2O_3$=5.0% by mol%, and mixing uniformly, It puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1400 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 540 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 850 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is $Li_{1+X}\text{aluminum}_X(\text{germanium}_{2-Y}Ti_Y)_{2-X}(PO_4)_3$. The crystallized glass showed high conductivity called 2.0×10^{-4}S/cm at the room temperature.

[0034][Examples 4-10] The sample of Examples 4-10 was produced by the same method as Example 2. The conductivity in the presentation and room temperature in each example was summarized in Tables 1 and 2. By alternating current impedance, the conductivity of crystallized glass was measured in the range of 10^{-2} - $3\times10^{+7}$Hz, asked for resistance (sum of resistance of particles and a grain boundary) of the sample from the call

call plot, and calculated conductivity according to equation sigma= (t/A) (1/R). (sigma: Conductivity, the thickness of t:sample, area of A:electrode, resistance of R:sample)

[0035]

[Table 1]

実施例No.	1	2	3	4	5
P_2O_5 (mol%)	37.5	37.5	37.5	37.5	37.5
SiO_2 (mol%)					
GeO_2 (mol%)	35.0	40.0	30.0	37.5	40.0
TiO_2 (mol%)			10.0		
ZrO_2 (mol%)					
Al_2O_3 (mol%)	7.5		5.0	4.5	5.0
Ga_2O_3 (mol%)		5.0		2.0	
Li_2O (mol%)	20.0	17.5	17.5	18.5	17.5
室温での伝導率 ($\times 10^{-4}$S/cm)	4.0	2.0	3.5	1.5	3.0

[0036]

[Table 2]

実施例No.	6	7	8	9	10
P_2O_5 (mol%)	39.0	39.0	39.0	33.0	33.0
SiO_2 (mol%)				5.0	8.0
GeO_2 (mol%)	37.5	33.0	35.5	37.5	11.0
TiO_2 (mol%)					30.0
ZrO_2 (mol%)				2.0	
Al_2O_3 (mol%)		11.0	6.0	4.5	5.0
Ga_2O_3 (mol%)	9.0		4.0		
Li_2O (mol%)	14.5	17.0	15.5	18.0	14.0
室温での伝導率 ($\times 10^{-4}$S/cm)	1.2	2.0	1.5	2.5	5.0

[0037][Example 11] An example (sectional view) of a flat type battery which used the lithium-ion-conductivity crystallized glass of Example 4 as a solid electrolyte is shown in drawing 2 as a typical example of a lithium cell. This cell The negative electrode can 6, the negative pole collector 4 (a conductive thin film, sheet metal, etc., such as aluminum and stainless steel, are used.), It consists of the negative electrode 2, the lithium-ion-conductivity crystallized glass 1, the anode 3, the positive pole collector 5 (a conductive thin film, sheet metal, etc., such as aluminum and stainless steel, are used.), the positive electrode can 7, the insulating packing 8 (product made from polypropylene), etc. Positive/negative each poles 2 and 3 are dedicated in the case which counters via lithium-ion-conductivity crystallized glass, and the positive-and-negative-poles cans 6 and 7 form. As for the anode 3, the negative electrode 2 is connected to the negative electrode can 6 via the negative pole collector 4 at the positive electrode can 7 via the positive pole collector 5. The chemical energy produced inside the cell can be taken out now from both the terminals of a positive electrode can and the negative electrode cans 6 and 7 to the exterior as electrical energy. About the member which constitutes the cell by this invention, it is possible except a solid electrolyte portion to use various materials which indicate above and are conventionally used besides the substance.

[0038]The thickness of lithium-ion-conductivity crystallized glass shall be thin, and shall be 0.5 mm or less preferably at least 1 mm or less here. Various kinds of devices and announcements are made and the material of the anode 3 has $LiCoO_2$, $Li_{1+X}V_3O_8$, etc. as a typical example. Various kinds of devices and announcements are similarly made about the material of the negative electrode 2, and there are $Li_4Ti_5O_{12}$, carbon, etc. as a typical example.
[0039]About positive/negative each poles 2 and 3 formed in both sides to which lithium-ion-conductivity crystallized glass counters, and the collectors 4 and 5 formed in positive/negative each pole. The method of making these which were created beforehand piling up mutually one by one, and attaching them, and a pole and a charge collector An ion spattering method, The method of forming one by one with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. can also be used.
[0040]A comparative example Titanium oxide:1.7 mol, lithium carbonate:0.7 mol, Ammonium phosphate : 3.0 mol and aluminum oxide:0.2 mol are mixed in an agate mortar, After carrying out pressing and making it a pellet type, the agate mortar ground again the fired material obtained by calcinating for 2 hours at 900 **, pressing of what passed the screen of 400 meshes was carried out to the pellet type, and what was sintered for 2 hours and processed laminated at 1000 ** was used as a solid electrolyte. The efficiency discharge characteristic figure of the cell of drawing 2 and the cell using the solid electrolyte of the comparative example is shown in drawing 4.
[0041][Example 12] An example (sectional view) of a carbonic acid gas sensor which used the lithium-ion-conductivity crystallized glass of Example 4 as a solid electrolyte is shown in drawing 3 as a typical example of a gas sensor. Up-and-down both sides of the Li-ion conductivity crystallized glass by the above-mentioned example to 1-2 mm in thickness, The mixture of a metallic carbonate layer, and desirable lithium carbonate or lithium carbonate and other carbonate is preferably formed in one side of the polished surface with an ion spattering method after grinding to 0.5 mm or less still more preferably 1 mm or less.
[0042]Subsequently, stick on this field the platinum mesh which connected the lead, a carbonate layer is made to form again, and a platinum mesh is fixed. The platinum thin film formed with vacuum deposition is formed in another field, and a lead is connected to this. Since the electromotive force according to carbon dioxide gas concentration arises in inter-electrode according to the dissociation equilibrium of carbonate by the carbon dioxide in a carbon dioxide gaseous mixture, this sensor can know carbon dioxide gas concentration rather than measuring this electromotive force.
[0043]The method of forming a carbonate layer and an electrode layer can be formed with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. besides the above. The electromotive force characteristic by the carbon dioxide partial pressure in the room temperature of this gas sensor is shown in drawing 5.
[0044]
[Effect of the Invention]As explained above, the lithium-ion-conductivity crystallized glass by this invention has very high lithium ion conductivity, and. Simply and chemically, since [stable] it is thermally strong, production begins a cell (a fuel cell is also included) and a gas sensor, and the application of it to various electrochemical devices is attained.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]Ionic conductivity of this invention is high, and is thermally and chemically stable, and manufacture is related with easy lithium-ion-conductivity crystallized glass.

[Translation done.]

PRIOR ART

[Description of the Prior Art]Progress of the electronics in recent years is remarkable, and the miniaturization of electronic equipment, a weight saving, and highly efficient-ization are progressing quickly. Then, as these power supplies for apparatus, development of a long lasting cell is strongly desired with high energy density, and the expectation for a lithium ion battery is large especially every day.

[0003]Since the oxidation-reduction potential of lithium elements of Li/Li^+ is the highest in all metal and the mass per mol is dramatically small, the lithium cell can obtain high energy density from other cells. By using a lithium ion conductive solid electrolyte, it becomes possible to make an electrolyte part thin, and the thin weight saving of the cell itself can be carried out, and it becomes possible to raise the energy density per volume greatly.

[0004]In addition to a miniaturization and thin-film-izing of a cell being difficult for the lithium ion battery put in practical use now, since an electrolyte is organic electrolysis liquid, we are anxious about liquid leakage or the danger of ignition. If it is transposed to an inorganic solid electrolyte, it will be thought that a reliable and extremely stable totally-solid battery can be constituted.

[0005]The choke damp emitted by combustion of a fossil fuel is the main factor of the greenhouse effect which poses a problem in recent years.
For this reason, the continuous surveillance of choke-damp concentration is needed.
Therefore, in order that establishment of these detection systems may maintain the comfortable living environment of future human society, the importance is increasing.

[0006]Although the choke-damp detection system with which practical use is presented has a common type using infrared absorption now, a device is large-sized, and is expensive and it has in contamination the fault that it is weak. Therefore, these days, research of the compact carbon dioxide gas sensor which used the solid electrolyte is done briskly. In it, many researches using a lithium ion solid electrolyte are reported.

[0007]However, in order to realize these, conductivity is high, it is chemically stable, and development of a solid electrolyte strong against heat is indispensable. As what conductivity is high in a solid electrolyte by the present, and exceeds 10^{-3}S/cm at a room temperature, A Li_3N single crystal [Applied PhysicsLetters, 30(1977)P.621-622], $LiI-Li_2S-P_2S_5$ [Solid State Ionics, 5(1981)P.663], $LiI-Li_2S-SiS_4$[J. Solid State Chem. and 69(1987)P.252], Although the glass of a $LiI-Li_2S-B_2S_3$ [Mat.Res.Bull., 18(1983)P.189] system is known, such materials are difficult to produce, chemical stability is not good, either, and heat has the fault that it is weak. Since decomposition voltage is low especially when using it as an electrolyte of a solid state battery, it has the fatal fault that high terminal voltage cannot be taken.

[0008]On the other hand, the possibility of utilization is high if a room temperature shows high conductivity, since an oxide lithium solid electrolyte does not have the above faults, and decomposition voltage is also higher than 3V. In oxide glass, increasing conductivity is known by increasing the concentration of a lithium ion. However, even if it uses rapid quenching for the purpose of vitrification, for example, there is a limit in the increase in the concentration of a lithium ion, and what has the high conductivity in a room temperature has not reached 10^{-6}S/cm.

[0009]Although JP,8-239218,A has the statement of the gas sensor which used the lithium-ion-conductivity glass thin film, That in which the conductivity of the lithium-ion-conductivity glass thin film by this has 6.1×10^{-7}S/cm from 1.7×10^{-7} and not a by no means high thing but higher conductivity is needed.

[0010]About oxide ceramics (sintered compact), many examples which have high lithium ion conductivity are

reported. A Li_4GeO_4-Li_3VO_4 system For example, 4x10 $^{-5}$S/cm [Mat.Res.Bull., 15(1980)P.1661], $Li_{1-X}M_XTi_{2-X}(PO_4)_3$ (M=aluminum, Ga, Cr, etc.) -- 7x10 $^{-4}$S/cm[-- J. -- Electrochem.Soc. and 137(1990)P.1023]. A Li_{1+X}aluminum$_X$germanium$_{2-X}(PO_4)_3$ system 1.3x10 $^{-4}$S/cm[Proceedings of 8 th international meetingon lithium. The conductivity in the room temperature batteries, June 16-21-1996, Nagoya, Japan, and P.316-317] is shown. Although oxide ceramics are advantageous in respect of conductivity compared with oxide glass, a manufacturing process is complicated and the moldability has the fault that it is bad and thin-film-izing is difficult.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]As explained above, the lithium-ion-conductivity crystallized glass by this invention has very high lithium ion conductivity, and. Simply and chemically, since [stable] it is thermally strong, production begins a cell (a fuel cell is also included) and a gas sensor, and the application of it to various electrochemical devices is attained.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]As stated above, the conventional lithium ion solid electrolyte had low conductivity, handling was difficult, and it had the technical problem that thin-film-izing was difficult. This invention solves these technical problems, the crystallized glass which has high lithium ion conductivity in a room temperature is provided, and it aims at realizing a highly efficient lithium cell and gas sensor further using this crystallized glass.

[Translation done.]

* NOTICES *

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damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem]As mentioned above, in ceramics, conductivity of a 10 $^{-4}$S/cm stand is found out at a room temperature. However, a stoma and a grain boundary which can never be lost exist in an inside of ceramics. These existence brings about decline in conductivity. Since a stoma can be lost and being improved also about a grain boundary will be expected if crystallized glass including a conductive crystal is obtained, it is expectable to obtain a solid electrolyte which has higher conductivity. Since various shape and thin film-ization are attained taking advantage of the characteristic of glass in the case of crystallized glass, a merit more practical than ceramics produced with a sintering process is large.
[0013]As a result of repeating research wholeheartedly based on such a view, this invention person P_2O_5, SiO_2, GeO_2, TiO_2, ZrO_2, and M_2O_3. Glass containing one sort chosen from M=aluminum and Ga or a (two-sort [however,]) Li_2O ingredient is produced, Through a heat treatment process by depositing conductive crystal $Li_{1+X}M_X$(germanium$_{1-Y}Ti_Y$) $_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) from glass, A lithium cell and a gas sensor which succeeded in obtaining crystallized glass which has high lithium ion conductivity in a room temperature, and used this came to find out that the good characteristic is shown.
[0014]Namely, the invention according to claim 1 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -50%, $TiO_2$0 -<50%, However, 25 to 50% of GeO_2+TiO_2, 0 to 10% of ZrO_2, One sort or two-sort $Li_2$0 chosen from 0.5 to 15% of M_2O_3 however M=aluminum, and Ga 10 to 25%, It is characterized by original glass containing a presentation of ****** depositing a $Li_{1+X}M_X$(germanium$_{1-Y}Ti_Y$) $_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0015]The invention according to claim 2 is mol%, and 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, 25 to 45% of $TiO_2$0 -<45%, however GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of aluminum$_2O_3$, $Li_2$0 Original glass containing a presentation of the range of 10 to 25%**, It is characterized by depositing a Li_{1+X}aluminum$_X$(germanium$_{1-Y}Ti_Y$) $_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0016]The invention according to claim 3 is mol%, and 35 to 40% of P_2O_5, 0 to 15% of SiO_2, $GeO_2$0< -45%, 25 to 45% of $TiO_2$0 -<45%, however GeO_2+TiO_2, 0 to 10% of ZrO_2, 0.5 to 15% of Ga_2O_3, $Li_2$0 Original glass containing a presentation of the range of 10 to 25%**, It is characterized by depositing a $Li_{1+X}Ga_X$ (germanium$_{1-Y}Ti_Y$) $_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase through a heat treatment process after melt molding, [0017]The invention according to claim 4 is characterized by using lithium-ion-conductivity crystallized glass of a statement for claims 1-3 in a solid electrolyte for lithium cells, [0018]The invention according to claim 5 is characterized by using lithium-ion-conductivity crystallized glass of a statement for claims 1-3 in a solid electrolyte for gas sensors, [0019]The invention according to claim 6 is characterized by using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3 in a lithium cell, [0020]The invention according to claim 7 is characterized by using lithium-ion-conductivity crystallized glass of a statement for a solid electrolyte at claims 1-3 in a gas sensor.
[0021]A presentation of crystallized glass of this invention can be displayed by an oxide basis like original glass. A reason which limited a presentation of crystallized glass as mentioned above is explained below.
[0022]Original glass containing the above-mentioned presentation through a heat treatment process after melting cooling by depositing a $Li_{1+X}M_X$(germanium$_{1-Y}Ti_Y$) $_{2-X}(PO_4)_3$ (0< X<=0.8, 0<=Y<1.0) crystal phase, With the

conventional ceramics, precise crystallized glass which is not obtained can be obtained and, moreover, the crystallized glass shows very high lithium ion conductivity with a room temperature. Although a $Li_{1+X}M_X$ (germanium$_{1-Y}$Ti$_Y$) $_{2-X}$(PO_4) $_3$ crystal phase deposits also in presentation fields other than the above, since the rate is very low, conductivity is small and application to practical use is difficult.

[0023]Also in the above-mentioned ingredient, especially M_2O_3 (one sort chosen from M=aluminum and Ga or two sorts), By being an important ingredient and adding this M_2O_3 ingredient 0.5 to 15% in an improvement of the melting nature of glass, and thermal stability, Melting nature and thermal stability of glass improved, and conductivity which exceeds 10^{-4}S/cm to a still more surprising thing in a composition range where conductivity of crystallized glass after heat treatment is also wide was shown. If an M_2O_3 ingredient is not filled to 0.5%, although vitrification is carried out, if melting nature and thermal stability of glass are bad and exceed 15%, On the contrary, melting nature falls, conductivity of crystallized glass after heat treatment also falls remarkably, and, below in 10^{-6}S/cm, conductivity becomes. A range in which said M_2O_3 ingredient is more preferred than ** is 1 to 14%, and especially a desirable range is 3 to 12%.

[0024]GeO_2 is an ingredient indispensable to formation of glass, and is also a constituent of a conductive crystal phase. if the amount of GeO_2 increases, although it becomes easy to form glass, since the effect is small, when the desired characteristic is not obtained but 50-mol% is exceeded conversely, said conductive crystal phase becomes difficult to deposit less than [25mol%] indeed. It is replaceable with TiO_2 and GeO_2 is possible for the substitutional rate to about 100%. And improvement in Li-ion conductivity is also found by substitution. They must be GeO_2=0<-50% from these things, TiO_2=0-<50%, however GeO_2+TiO_2=25-50%. a desirable range -- GeO_2=0<-45% and TiO_2=0-<45% -- however, It is GeO_2+TiO_2=25-45% and especially desirable ranges are GeO_2=0<-40%, TiO_2=0-<40%, however GeO_2+TiO_2=28-40%.

[0025]While the addition of SiO_2 can raise thermal stability of original glass, Si^{4+} ion dissolves to said crystal phase, and contributes it also to improvement in Li^+ ionic conductivity. However, since conductivity will fall on the contrary if the quantity exceeds 15%, it must be made to 15% or less. A desirable range is 13% or less, and especially a desirable range is 10% or less.

[0026]Addition of ZrO_2 has an effect which promotes generation of this crystal phase. However, since the devitrification-proof nature of original glass falls remarkably, creation of uniform original glass will become difficult and also conductivity will also fall rapidly if the quantity exceeds 10%, it must be made to 10% or less. A desirable range is 8% or less, and especially a desirable range is 5% or less.

[0027]Although it is also possible to be divalent metals, such as trivalent metals, such as B, In, Sc, Fe, and Cr, and Mg, Ca, Sr, Ba, and Zn, and to replace a part of aluminum or Ga ingredient, those quantity should be made less than 10mol%. If it adds more, production of original glass will become difficult or conductivity will fall remarkably.

[0028]In order to improve the melting nature of glass further, it is also possible to add As_2O_3, Sb_2O_3, Ta_2O_3, CdO, PbO, etc., but those quantity should be restricted to 3% or less. Addition of more than it will reduce conductivity remarkably in connection with an addition.

[0029]

[Embodiment of the Invention]The lithium-ion-conductivity crystallized glass of this invention can be manufactured by the following methods. That is, after carrying out specified quantity weighing of each starting material and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. In heating and dissolving, a raw material is first disassembled at 700 **, and gas constituents are evaporated. Next, temperature is raised to 1300-1450 **, and at the temperature, it holds for 1 to 2 hours, and dissolves. Then, the cast of the melting glass is carried out on a griddle, and tabular glass is produced. In this way, the obtained glass is heat-treated at 600-1000 ** for 12 to 24 hours. By the above process, the crystallized glass with high lithium ion conductivity in which $Li_{1+X}M_X$(germanium$_{1-Y}$Ti$_Y$) $_{2-X}$(PO_4) $_3$ deposited as a main crystal phase is obtained.

[Translation done.]

EXAMPLE

[Example]This invention is not limited by these examples although a concrete example explains this invention below.

[0031][Example 1] $NH_4H_2PO_4$, GeO_2, aluminum$(OH)_3$, and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 20.0% of Li_2 P_2O_5=37.5%, GeO_2=35.0%, and aluminum$_2O_3$=7.5% by mol%, and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1300 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 520 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 750 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is Li_{1+X}aluminum$_X$germanium$_{2-X}(PO_4)_3$. It is shown in drawing 1 of the X diffraction pattern of this crystallized glass. The crystallized glass showed high conductivity called 4.0×10^{-4}S/cm at the room temperature.

[0032][Example 2] $NH_4H_2PO_4$, GeO_2, and Ga_2O_3 and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 17.5% of Li_2 P_2O_5=37.5%, GeO_2=40.0%, and Ga_2O_3=5.0% by mol%, and mixing uniformly, it puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1300 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 510 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 800 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is $Li_{1+X}Ga_X$germanium$_{2-X}(PO_4)_3$. The crystallized glass showed high conductivity called 2.0×10^{-4}S/cm at the room temperature.

[0033][Example 3] $NH_4H_2PO_4$, GeO_2, TiO_2, and aluminum$_2O_3$ and Li_2CO_3 are used as a raw material. After carrying out weighing of these so that it may become the presentation of O= 17.5% of Li_2 P_2O_5=37.5%, GeO_2=30.0%, TiO_2=10%, and aluminum$_2O_3$=5.0% by mol%, and mixing uniformly, It puts into a platinum crucible and heating and dissolving are carried out with an electric furnace. Here, first, a raw material is disassembled at 700 ** and CO_2, NH_3, and an H_2O ingredient are evaporated. Next, temperature up is carried out to 1400 **, and it dissolves at the temperature for 1.5 hours. Then, the cast is carried out on the griddle which warmed dissolution glass beforehand, and uniform tabular glass is produced. And in order to remove distortion of glass, it annealed at 540 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by performing heat treatment at 850 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is Li_{1+X}aluminum$_X$(germanium$_{2-Y}Ti_Y)_{2-X}(PO_4)_3$. The crystallized glass showed high conductivity called 2.0×10^{-4}S/cm at the room temperature.

[0034][Examples 4-10] The sample of Examples 4-10 was produced by the same method as Example 2. The conductivity in the presentation and room temperature in each example was summarized in Tables 1 and 2. By alternating current impedance, the conductivity of crystallized glass was measured in the range of 10^{-2} - $3\times10^{+7}$Hz, asked for resistance (sum of resistance of particles and a grain boundary) of the sample from the call call plot, and calculated conductivity according to equation sigma= (t/A) (1/R). (sigma: Conductivity, the thickness of t:sample, area of A:electrode, resistance of R:sample)

[0035]

[Table 1]

実施例No.	1	2	3	4	5
P_2O_5 (mol%)	37.5	37.5	37.5	37.5	37.5
SiO_2 (mol%)					
GeO_2 (mol%)	35.0	40.0	30.0	37.5	40.0
TiO_2 (mol%)			10.0		
ZrO_2 (mol%)					
Al_2O_3 (mol%)	7.5		5.0	4.5	5.0
Ga_2O_3 (mol%)		5.0		2.0	
Li_2O (mol%)	20.0	17.5	17.5	18.5	17.5
室温での伝導率 ($\times10^{-4}$S/cm)	4.0	2.0	3.5	1.5	3.0

[0036]

[Table 2]

実施例No.	6	7	8	9	10
P_2O_5 (mol%)	39.0	39.0	39.0	33.0	33.0
SiO_2 (mol%)				5.0	8.0
GeO_2 (mol%)	37.5	33.0	35.5	37.5	11.0
TiO_2 (mol%)					30.0
ZrO_2 (mol%)				2.0	
Al_2O_3 (mol%)		11.0	6.0	4.5	5.0
Ga_2O_3 (mol%)	9.0		4.0		
Li_2O (mol%)	14.5	17.0	15.5	18.0	14.0
室温での伝導率 ($\times10^{-4}$S/cm)	1.2	2.0	1.5	2.5	5.0

[0037][Example 11] An example (sectional view) of a flat type battery which used the lithium-ion-conductivity crystallized glass of Example 4 as a solid electrolyte is shown in drawing 2 as a typical example of a lithium cell. This cell The negative electrode can 6, the negative pole collector 4 (a conductive thin film, sheet metal, etc., such as aluminum and stainless steel, are used.), It consists of the negative electrode 2, the lithium-ion-conductivity crystallized glass 1, the anode 3, the positive pole collector 5 (a conductive thin film, sheet metal, etc., such as aluminum and stainless steel, are used.), the positive electrode can 7, the insulating packing 8 (product made from polypropylene), etc. Positive/negative each poles 2 and 3 are dedicated in the case which counters via lithium-ion-conductivity crystallized glass, and the positive-and-negative-poles cans 6 and 7 form. As for the anode 3, the negative electrode 2 is connected to the negative electrode can 6 via the negative pole collector 4 at the positive electrode can 7 via the positive pole collector 5. The chemical energy produced inside

the cell can be taken out now from both the terminals of a positive electrode can and the negative electrode cans 6 and 7 to the exterior as electrical energy. About the member which constitutes the cell by this invention, it is possible except a solid electrolyte portion to use various materials which indicate above and are conventionally used besides the substance.
[0038]The thickness of lithium-ion-conductivity crystallized glass shall be thin, and shall be 0.5 mm or less preferably at least 1 mm or less here. Various kinds of devices and announcements are made and the material of the anode 3 has $LiCoO_2$, $Li_{1+X}V_3O_8$, etc. as a typical example. Various kinds of devices and announcements are similarly made about the material of the negative electrode 2, and there are $Li_4Ti_5O_{12}$, carbon, etc. as a typical example.
[0039]About positive/negative each poles 2 and 3 formed in both sides to which lithium-ion-conductivity crystallized glass counters, and the collectors 4 and 5 formed in positive/negative each pole. The method of making these which were created beforehand piling up mutually one by one, and attaching them, and a pole and a charge collector An ion spattering method, The method of forming one by one with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. can also be used.
[0040]A comparative example Titanium oxide:1.7 mol, lithium carbonate:0.7 mol, Ammonium phosphate : 3.0 mol and aluminum oxide:0.2 mol are mixed in an agate mortar, After carrying out pressing and making it a pellet type, the agate mortar ground again the fired material obtained by calcinating for 2 hours at 900 **, pressing of what passed the screen of 400 meshes was carried out to the pellet type, and what was sintered for 2 hours and processed laminated at 1000 ** was used as a solid electrolyte. The efficiency discharge characteristic figure of the cell of drawing 2 and the cell using the solid electrolyte of the comparative example is shown in drawing 4.
[0041][Example 12] An example (sectional view) of a carbonic acid gas sensor which used the lithium-ion-conductivity crystallized glass of Example 4 as a solid electrolyte is shown in drawing 3 as a typical example of a gas sensor. Up-and-down both sides of the Li-ion conductivity crystallized glass by the above-mentioned example to 1-2 mm in thickness, The mixture of a metallic carbonate layer, and desirable lithium carbonate or lithium carbonate and other carbonate is preferably formed in one side of the polished surface with an ion spattering method after grinding to 0.5 mm or less still more preferably 1 mm or less.
[0042]Subsequently, stick on this field the platinum mesh which connected the lead, a carbonate layer is made to form again, and a platinum mesh is fixed. The platinum thin film formed with vacuum deposition is formed in another field, and a lead is connected to this. Since the electromotive force according to carbon dioxide gas concentration arises in inter-electrode according to the dissociation equilibrium of carbonate by the carbon dioxide in a carbon dioxide gaseous mixture, this sensor can know carbon dioxide gas concentration rather than measuring this electromotive force.
[0043]The method of forming a carbonate layer and an electrode layer can be formed with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. besides the above. The electromotive force characteristic by the carbon dioxide partial pressure in the room temperature of this gas sensor is shown in drawing 5.
[0044]

[Translation done.]

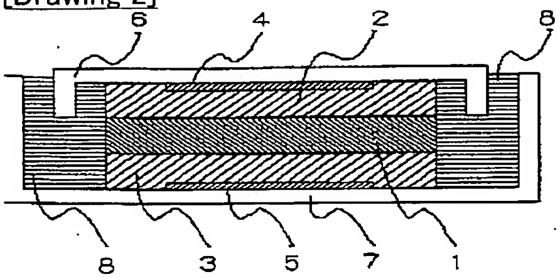
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The X diffraction pattern of the crystallized glass of Example 1 is shown.
[Drawing 2]It is a figure showing a typical structure of the lithium cell which uses the lithium ion solid electrolyte by Example 2 of this invention.
[Drawing 3]It is a figure showing a typical structure of the gas sensor which uses the lithium ion solid electrolyte by Example 2 of this invention.
[Drawing 4]It is an efficiency discharge characteristic figure of the cell shown in drawing 2.
[Drawing 5]It is an electromotive force characteristic figure by the carbon dioxide partial pressure in the room temperature of the gas sensor shown in drawing 3.
[Description of Notations]
1, lithium-ion-conductivity crystallized glass
2, a negative electrode
3, an anode
4, a negative-electrode collecting electrode plate
5, an anode current collector
6, a negative electrode can
7, a positive electrode can
8, insulating packing
9, metallic carbonate
10 Electrode
11, lithium-ion-conductivity crystallized glass
12 Electrode
13 Lead
14 Lead
15, package material

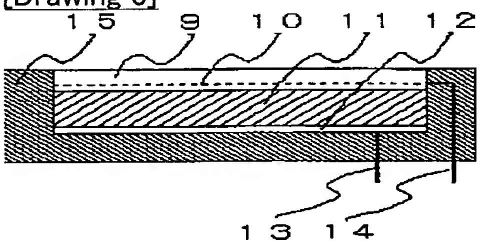
[Translation done.]

DRAWINGS

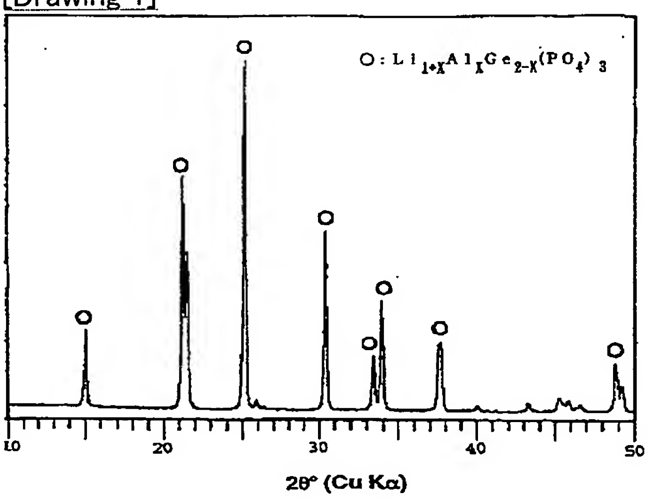
[Drawing 2]



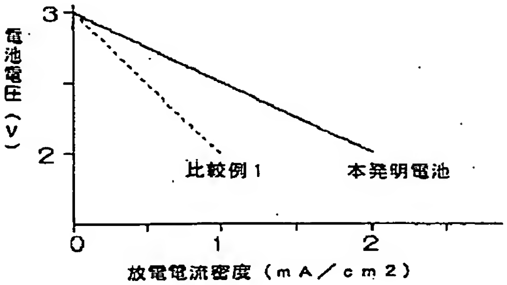
[Drawing 3]



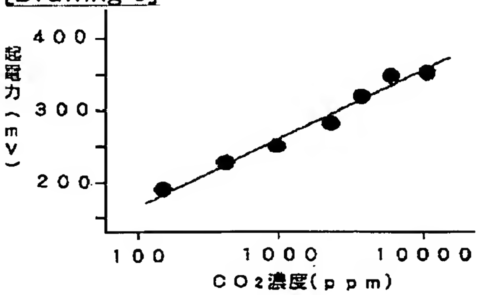
[Drawing 1]



[Drawing 4]



[Drawing 5]



[Translation done.]